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Elastic Properties of $(CsCN)_x(CsX)_{1-x}$, Mixed Crystal

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ABSTRACT

The TOEC's elastic characteristics of mixed alkali cyanide-alkali halide crystal $(CsCN)_x(CsX)_{1-x}$ (X= Cl) for x=0, 0.28, 0.59, and 0.96 at various temperatures have been examined using an Extended three-body force shell model (ETSM). The effect of coupling between the cyanide molecules' rotational and translational motion is included in this model. Finite elasticity, in which elastic stress is non-linear with elastic strain, is the responsibility of the TOECs. In some crystallographic planes, the elastic shear behaviour is asymmetric with regard to shear displacements. The knowledge of ion-core repulsive interactions; which vary with the interatomic separation; is related to the third order elastic constants.

Keywords: Elastic constants; Stress; Repulsive interaction; Elastic softening; Mixed crystals; Translational-rotational coupling; Pauling coefficient; Model parameters; Disordered crystals; Static; Dynamic; Dielectric.

1. Introduction

Mixed crystals of the type $A(CN)_xX_{1-x}$, where A is an alkali metal ion (K, Rb, Na, Cs etc.) and X is a halogen ion (Br or Cl) have been a subject of extensive research during recent years. The $(CsCN)_x(CsX)_{1-x}$, (X= Cl) mixed crystals offer a useful system for understanding the importance of the translational-rotational coupling in orientationally disordered crystal. These orientationally disordered crystals have shown significant effects that are attributed to the TR coupling. By altering the substitutional disorder in mixed crystals, the effect of translational rotational coupling can be varied [1]. It affects both the phonon and elastic characteristics at finite wave vector, which can result in lattice instability or even an orientational glass state [2,3]. Specifically, there is a substantial coupling between CN-orientational modes and transverse acoustic (TA) lattice translational modes [4].

In addition to being interesting in and of themselves, elastic constants of crystals and their temperature dependence offer significant insight into the interatomic forces of solids [5].

In order to account for the impact of coupling between the translational and rotational modes of CN-molecules, we have created an Extended Three-Body Force Shell Model (ETSM) [6,7]. The static, dynamic, dielectric, optical, and anharmonic characteristics of pure ionic crystals have all been effectively studied using this model. In the present work, we extend the application of the ETSM to calculate the third order elastic constant (TOECs) for mixed $(CsCN)_x(CsX)_{1-x}$ (X= Cl) for x=0, 0.28, 0.59 and 0.96 at different temperature.

1.1. Study Objectives

The main objectives of this research paper are:

1. To study of elastic, third order elastic constants of orientationally disordered mixed crystals at various temperatures.

2. To develop an Extended Three Body Force Shell Model incorporated by TR coupling.

3. To compute TR coupling coefficients and Van der waal coefficients. To write a computer program for the calculation of elastic, cohesive, thermal and dynamical properties.

4. Application of ETSM to study the elastic properties as a function of temperature.

2. Essential Formalism

The interaction potential that was utilised to create the current ETSM's architecture is represented as [8-10]:

$$\phi = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1}\left[1+\sum_{k'} f_k(r_{kk'})\right] - \sum_{k'} c_{kk'} r_{kk'}^{-6} - \sum_{k'} d_{kk'} r_{kk'}^{-8} - b\sum_{k'} \beta_{kk'} \exp\left\{\frac{r_k + r_{k'} - r_{kk'}}{\rho}\right\} + \phi^{TR} \quad (1)$$

where the first two terms represent the long range Coloumb and Three Body Interaction [13]; the third and fourth terms are the van der Waals (vdW) interaction due to dipole-dipole(d-d) and dipole-quadrapole(d-q) attractions, the fifth term represents the Hafemeister Flygare [8] type short-range overlap repulsion extended up to second neighbour ions, $\beta_{kk'}$ are the Pauling coefficient, ρ and b are the range and hardness model parameters, respectively as defined earlier [11-13]:

$$\left[\frac{d\phi(r)}{dr}\right]_{r=r_0} = 0 \quad (2)$$

and the bulk modulus,

$$B = \frac{1}{9Kr_0}\left[\frac{d^2\phi(r)}{dr^2}\right]_{r=r} \quad (3)$$

ϕ^{TR} is the contribution due to TR coupling effects Where r is the nearest neighbour (nn) sepration and r_o is the equilibrium nn separation. K as the crystal structure constant. The TR coupling effect has been taken through elastic constant. The temperature dependent Third Order Elastic Constants (TOECs) are determined with the help of following equations:

$$c_{111} = -26.9198Tb\beta_T + \frac{e^2}{4r_0^4}[12.1266B_1 + \frac{C_1 - 3A_1}{18} + 13.4599B_1 + \frac{C_2 - 3A_2}{2} + 2.7138\varepsilon r_0^2 f''(r_0) + 13.1567\varepsilon r_0 f'(r_0)] \quad (4)$$

$$c_{112} = 4.1279Tb\beta_T + \frac{e^2}{4r_0^4}[-1.8973B_1 + \frac{C_1 - 3A_1}{18} - 2.064B_2 + 2.7138\varepsilon r_0^2 f''(r_0) - 6.2677\varepsilon r_0 f'(r_0)] \quad (5)$$

$$c_{166} = 2.1279Tb\beta_T + \frac{e^2}{4r_0^4}[-1.8973B_1 + \frac{C_1 - 3A_1}{18} - 2.064B_2 + 0.904\varepsilon r_0^2 f''(r_0) + 5.3266\varepsilon r_0 f'(r_0)] \quad (6)$$

$$c_{123} = 7.0755Tb\beta_T + \frac{e^2}{4r_0^4}[-3.3711B_1 + \frac{C_1 - 3A_1}{18} - 3.5377B_2 + 2.7138\varepsilon r_0^2 f''(r_0) - 15.9799\varepsilon r_0 f'(r_0)] \quad (7)$$

$$c_{144} = 7.0755Tb\beta_T + \frac{e^2}{4r_0^4}[-3.3711B_1 + \frac{C_1 - 3A_1}{18} - 3.5377B_2 + 0.904\varepsilon r_0^2 f''(r_0) - 5.3266\varepsilon r_0 f'(r_0)] \quad (8)$$

$$c_{456} = 7.0755Tb\beta_T + \frac{e^2}{4r_0^4}[-3.3711B_1 + \frac{C_1 - 3A_1}{18} - 3.5377B_2] \quad (9)$$

where $T\beta B_T = \frac{e^2}{4r^4}[1.165\varepsilon\{\varepsilon + 12f(r)\} + B_1 + B_2]$

and A_1, A_2, B_1, B_2 are the short range force parameters; f(r) and rf'(r) are the TBI parameters. The parameter f(r) and its derivatives are calculated from the knowledge of elastic constants and the relation $f = f_0 \exp(-r/\rho)$. The TOECs are obtained from equation (4) to (9) incorporated by TR coupling.

3. Result and Discussion

The input data for $(CsCN)_x(CsCl)_{1-x,}$ [14-18] at different temperature are obtained from pure CsCN, and CsCl, by the well known Vegards law [19]. To calculate r_0 at different composition at x=0, 0.28, 0.59 and 0.96 as,

$$r_0[(MCN)_x(MX)_{1-x}] = xr_0[(MCN)] + (1-x)r_0[(MX)] \quad (10)$$

Where x and 1-x are concentration dependent parameters for the host and substituted ions respectively. To obtain data at different temperature, we have used the thermal expansion relation,

$$I_T = I_o(1+\alpha T) \quad (11)$$

The calculated values of the input data for various concentrations are given in Table 1 where all the symbols have the usual meanings as explained earlier.

Table 1. Input data and vdW coefficient for $(CsCN)_x(CsCl)_{1-x}$ at room temperature

Properties	**$(CsCN)_x(CsCl)_{1-x}$**			
Concentration	**x=0**	**x=0.28**	**x=0.59**	**x=0.96**
r_0 (Å)	3.571	3.602	3.635	3.676
r_+	1.903	1.903	1.903	1.903
r_-	1.648	1.682	1.72	1.765
c_{11} (10^{11}dyn cm^{-2})	3.640	3.209	2.731	2.162
c_{12} (10^{11}dyn cm^{-2})	0.920	1.026	1.144	1.285
c_{44} (10^{11}dyn cm^{-2})	0.800	0.688	0.564	0.416
α_+(Å)^3	1.140	1.5198	2.438	3.252
α_- (Å)^3	4.130	2.2876	2.755	1.893

Using the above input data, we have calculated the model parameters of these systems. The model parameters viz. interatomic separation (r), hardness parameter (b), range parameter (ρ) and three body interaction parameter rf(r_0) were calculated for various temperature The values for these four model parameters along with corresponding inter atomic separation at different concentration x=0, 0.28, 0.59 and 0.96 are given in Tables 2 and 3.

Table 2. Model parameters for **$(CsCN)_x(CsX)_{1-x}$ (X= Cl)** at x=0, 0.28, 0.59 and 0.96

T(K)	ρ_o		ρ	
	x=0	**x=0.28**	**x=0**	**x=0.28**
300	3.619	3.650	0.359	0.347
	x=0.59	**x=0.96**	**x=0.59**	**x=0.96**
300	3.684	3.725	0.354	0.357

Table 3. Model parameters for **$(CsCN)_x(CsX)_{1-x}$ (X= Cl)** at x=0, 0.28, 0.59 and 0.96

T(K)	b		f(r)	
	x=0	**x=0.28**	**x=0**	**x=0.28**
300	0.260	0.397	-0.006	-0.017
	x=0.59	x=0.96	x=0.59	x=0.96
300	0.564	0.771	-0.031	-0.048

4. Third Order Elastic Constants

Thus far, we have examined how translational-rotational interaction in perfect periodic crystals softens elastic constants. It is feasible to alter the substitutional disorder in a mixed crystal to change the significance of TR coupling. The most prominent example of this category of mixed crystals are the alkali metal halide cyanides $CsCN_xX_{1-x}$. Here, X is a halogen. These systems have extremely rich phase diagrams, depending on the concentration and kind of substitutional ion.

ETSM has provided a theoretical explanation in terms of TR coupling. The translation-rotation coupling at the zone centre reduces (or softens) elastic constants in orientationally disordered CsCN-CsX mixed crystals. In the event that this coupling leads to a more ordered state, the corresponding elastic constant's softening will be strongly and anomalously temperature dependent, declining as the temperature is lowered towards Tc.

However, translation-rotation coupling that is not involved in the phase transition can still significantly soften elastic constants in orientationally disordered phases where the phase transition does not occur at the zone centre. In this section we will compute the third order elastic constants of $(CsCN)_x(CsCl)_{1-x}$, for different temperature range, for the concentrations x=0, 0.28, 0.59 and 0.96. The translational-rotational coupling of the CN^- ion is taken into account. The TR coupling is applied on the lines of Sahu and Mahanti [20].

We have calculated the third order elastic constants at different concentration and temperature with the help of equations 4-9. The results obtained from ETSM for third order elastic constant are shown in Table 4(a) to Table 4(d) for $(CsCN)_x(CsCl)_{1-x}$.

Table 4(a). TOECs (in the units 10^{12}dynes/cm^2) for $(CsCN)_x(CsCl)_{1-x,}$ at x=0 in the temperature range 50K ≤ T ≤ 300K

T(K)	c_{111}	c_{112}	c_{166}	c_{123}	c_{144}	c_{456}
50	-2.653	-0.128	-0.093	-0.151	-0.097	-0.083
100	-2.637	-0.128	-0.093	-0.152	-0.097	-0.083
150	-2.619	-0.129	-0.094	-0.152	-0.098	-0.084
200	-2.603	-0.129	-0.094	-0.153	-0.098	-0.084
250	-2.587	-0.129	-0.094	-0.153	-0.098	-0.084
300	-2.570	-0.129	-0.095	-0.153	-0.099	-0.085

Table 4(b). TOECs (in the units 10^{12}dynes/cm^2) for $(CsCN)_x(CsCl)_{1-x}$ at x=0.28 in the temperature range 50K ≤ T ≤ 300K

T(K)	c_{111}	c_{112}	c_{166}	c_{123}	c_{144}	c_{456}
50	-4.042	-0.283	-0.202	-0.326	-0.226	-0.186
100	-4.027	-0.284	-0.203	-0.327	-0.227	-0.187
150	-4.011	-0.285	-0.204	-0.327	-0.227	-0.188
200	-3.995	-0.285	-0.205	-0.328	-0.228	-0.188
250	-3.980	-0.286	-0.205	-0.328	-0.229	-0.189
300	-3.965	-0.286	-0.206	-0.329	-0.229	-0.189

Table 4(c). TOECs (in the units 10^{12}dynes/cm^2) for $(CsCN)_x(CsCl)_{1-x,}$ at x=0.59 in the temperature range 50K ≤ T ≤ 300K

T(K)	c_{111}	c_{112}	c_{166}	c_{123}	c_{144}	c_{456}
50	-5.272	-0.441	-0.310	-0.507	-0.357	-0.289
100	-5.258	-0.442	-0.312	-0.508	-0.358	-0.289
150	-5.245	-0.443	-0.313	-0.509	-0.359	-0.290
200	-5.232	-0.444	-0.314	-0.509	-0.359	-0.292
250	-5.219	-0.445	-0.315	-0.511	-0.361	-0.292
300	-5.207	-0.446	-0.316	-0.511	-0.362	-0.294

Table 4(d). TOECs (in the units 10^{12}dynes/cm^2) for $(CsCN)_x(CsCl)_{1-x,}$ at x=0.96 in the temperature range 50K ≤ T ≤ 300K

T(K)	c_{111}	c_{112}	c_{166}	c_{123}	c_{144}	c_{456}
50	-6.600	-0.637	-0.44	-0.729	-0.5195	-0.417
100	-6.589	-0.638	-0.44	-0.731	-0.5210	-0.419
150	-6.578	-0.640	-0.45	-0.732	-0.5225	-0.420
200	-6.567	-0.642	-0.45	-0.734	-0.5240	-0.421
250	-6.557	-0.643	-0.45	-0.735	-0.5254	-0.423
300	-6.546	-0.645	-0.45	-0.737	-0.5269	-0.424

5. Conclusion and Future Suggestions

It can be clearly seen from the above Tables 4(a) to 4(d) that the value of third order elastic constant c_{111} decreases with concentration while all other quantities of $(CsCN)_x(CsCl)_{1-x}$ crystals increases with increase in temperature. At

x=0 except c_{111} all other quantities show a quasi linear behaviour, for other concentration it shows same trend as followed by $(CsCN)_x(CsCl)_{1-x}$. This paper is the systematic and comprehensive theoretical investigation of thermoelastic properties of orientationally disordered mixed crystals. The motivation for the present work stems from the fact that large amount of experimental work has been done but a few theoretical attempts have been made to investigate the effect of orientational disorder on the fundamental properties of these materials. This work will serve as a catalyst and guide for experimentalist and for future researches.

Declarations

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Competing Interests Statement

The author declares having no competing interest with any party concerned during this publication.

Consent for Publication

The author declares that she consented to the publication of this study.

Authors' contributions

All research work is from the author.

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